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HALOGEN-CONTAINING RESINS STABILIZED WITH A TIN COMPOUND AND A LIQUID POLYTHIOPOLYMERCAPTAN

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The present invention relates to the preparation of halogen containing resins containing tin compounds as stabilizers therefor.

It is an object of the present invention to extend the heat and light stability of halogen containing resins.

Another object is to provide novel stabilized vinyl resin compositions.

Still further objects and the entire scope of applicability of the present invention will become apparent from the detailed description given hereinafter; it should be understood, however, that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

It has now been found that these objects can be attained by employing a mixture of a tin stabilizer and a nontin containing sulfur compound from the group of (1) a liquid polythiopolymercaptan and (2) alkylene glycol and polyethylene glycol derivatives of 3-mercaptopropionic acid, mercaptoacetic acid or 4-mercaptobutyric acid as heat and light stabilizers for halogen containing resins. It has been found that the use of the mixture of tin compound and nontin containing sulfur compound exerts a synergistic stabilizing action which could not be foretold from the use of either of these alone.

In the specification and claims all parts and percentages are by weight unless otherwise indicated.

The stabilizers of the present invention can be used with halogen containing vinyl and vinylidene resins in which the halogen is attached directly to the carbon atoms. Preferably, the resin is a vinyl halide resin, specifically, a vinyl chloride resin. Usually, the vinyl chloride resin is made from monomers consisting of vinyl chloride alone or a mixture of monomers comprising at least 70% vinyl chloride by weight. When vinyl chloride copolymers are stabilized, preferably the copolymer of vinyl chloride with an ethylenically unsaturated compound copolymerizable therewith contains at least 10% of polymerized vinyl chloride.

As the chlorinated resin there can be employed chlorinated polyethylene having 14 to 75%, e.g., 27%, chlorine by weight, polyvinyl chloride, polyvinylidene chloride, polyvinyl bromide, polyvinyl fluoride, copolymers of vinyl chloride with 1 to 90%, preferably 1 to 30%, of a copolymerizable ethylenically unsaturated material such as vinyl acetate, vinyl butyrate, vinyl benzoate, vinylidene chloride, diethyl fumarate, diethyl maleate, other alkyl fumarates and maleates, vinyl propionate, methyl acrylate, 2-ethylhexyl acrylate, butyl acrylate and other alkyl acrylates, methyl methacrylate, ethyl methacrylate, butyl methacrylate and other alkyl methacrylates, methyl alpha chloroacrylate, styrene, trichloroethylene, vinyl ethers such as vinyl ethyl ether, vinyl chloroethyl ether and vinyl phenyl ether, vinyl ketones such as vinyl methyl ketone and vinyl phenyl ketone, 1-fluoro-1-chloroethylene, acrylonitrile, chlor acrylonitrile, allylidene diacetate and chloroallylidene diacetate. Typical copolymers include vinyl chloride-vinyl acetate (96:4 sold commercially as VYNW), vinyl chloride-vinylacetate (87:13), vinyl chloride-vinyl acetate-maleic anhydride (86:13:1), vinyl chloride-vinylidene chloride (95:5), vinyl chloride-diethyl fumarate (95:5), vinyl chloride-trichloroethylene (95:5), vinyl chloride-2-ethylhexyl acrylate (80:20).

The mixture of stabilizers of the present invention can be incorporated with the resin by admixing in an appropriate mill or mixer or by any of the other well known methods which provide for uniform distribution throughout the resin compositions. Thus, mixing can be accomplished by milling on rolls at 100–160° C.

In addition to the novel mixture of stabilizers there can also be incorporated with the resin conventional additives such as plasticizers, pigments, fillers, dyes, ultraviolet light absorbing agents, densifying agents and the like.

If a plasticizer is employed, it is used in conventional amount, e.g., 30 to 150 parts per 100 parts of resin. Typical plasticizers are di-2-ethylhexyl phthalate, dibutyl sebacate, dioctyl sebacate, tricresyl phosphate.

The tin compound in the stabilizer mixture is normally used in an amount of 0.01 to 10% by weight of the resin and the sulfur compound also is normally used in an amount of 0.01 to 10% by weight of the resin. More preferably, 0.2 to 5% of the tin compound and 0.2 to 5% of the sulfur compound are employed based on the weight of the resin.

As the tin compound there can be employed any tin stabilizers for halogen containing resins. Typical examples of such compounds have the formulae $RSnX_3$, R_2SnX_2 and R_3SnX where R is a univalent organic radical such as alkyl, aryl, aralkyl or substituted derivatives and X is —OR, RCOO—, ROOCR'COO—, —SR, —OOCR'SH or ROOCR'S— wherein R is as defined above and R' is a divalent organic radical, usually alkylene. The various R groups can be the same or different. In addition, two X's together can be a divalent radical such as —OOCR'COO—.

Furthermore, there can be employed compounds such as R_2SnO and R_2SnS.

Illustrative examples of tin compounds which can be employed include dibutyl tin dibutoxide, dibutyl tin dilaurate, dibutyl tin bis butylazealate, dibutyl tin dioctyl mercaptide, 2,2 - dioctyl - 1-oxa-2-stanna-3-thiocyclopentane-5-one, dibutyl tin bis butylmercaptoacetate, dibutyl tin bis monobutyladipate, dioctyl tin bis isooctylmercaptoacetate, dioctyl tin oxide, dibutyl tin sulfide, diphenyl tin oxide, dibenzyl tin oxide, dilauryl tin oxide, methyl phenyl tin oxide, butyl stannoic acid, dioctyl tin sulfide, 2,2-dibutyl-1-oxa-2-stanna-3-thiocyclopentane - 5 - one, dioctyl tin dibutoxide, dioctyl tin dioctoxide, butyl tin tributoxide, dimethyl tin dicoconut mercaptide, dibutyl tin distearyl mercaptide, butyl tin tridodecyl mercaptide, diethyl tin dicresyl mercaptide, octyl tin triphenyl mercaptide, phenyl tin tributyl mercaptide, trioctyl tin butoxide, trimethyl tin octoxide, triphenyl tin butoxide, methyl tin tricoconut mercaptide, dibutyl tin dithioglycolic acid cyclohexyl ester, monobutyl tin trithiopropionic acid hexyl ester, triphenyl tin thioglycolic acid benzyl ester, dilauryl tin dithiobutyric acid amyl ester, dipropyl tin dithiovaleric acid tetrahydrofurfuryl ester, butyl tin tris (mercapt acetic acid), dibutyl tin S,S' bis (dibutyl thiomalate), dibutyl tin S,S' bis (thiomalic acid), and dibutyl tin maleate.

These tin compounds have the characteristic f being acceptors for hydrogen chloride and hence act as stabilizers.

As the synergistic nontin c ntaining sulfur compound there can be empl yed polythi polymercaptans having a molecular weight f 250 or preferably 500 t 12,000, and existing at 25° C. as a liquid. These materials are available commercially as various f rms of liquid Thio-

LP-8 with dibutyl tin bis mon butyl maleate as the tin stabilizer for vinyl chloride resins. In each case there was used 100 parts of resin, 50 parts f plasticizer, 1.8 parts of dibutyl tin bis monobutyl maleate and the indicated amount of Thiokol LP-8.

Resin	Plasticizer	Thiokol LP-8, parts	Heat Stability at 355° F. (minutes)
Geon 103EP	Dioctyl phthalate	0	45
Geon 103EP	do	0.25	75
Geon 103EP	do	1.00	90
VYNW	do	none	45
VYNW	do	0.25	60
VYNW	do	1.00	75
Geon 103EP	Tricresyl phosphate	0	30
Geon 103EP	do	0.60	60

It is clear from the table that Thiokol LP-8 definitely improves the stabilizing action of dibutyl tin bis monobutyl maleate.

We claim:

1. A composition of matter comprising a halogen containing resin selected from the group consisting of vinyl and vinylidene resins in which the halogen is attached directly to the carbon atoms in the polymer chain and a mixture of 0.01 to 10% of an organo tin stabilizer for said resin and 0.01 to 10% of a liquid polythiopolymercaptan.

2. A composition according to claim 1 wherein said sulfur compound is a liquid polydithiopolymercaptan.

3. A composition according to claim 1 wherein said resin is a vinyl chloride resin.

4. A composition according to claim 1 wherein the halogen containing resin is a vinyl chloride resin and the organo tin stabilizer is a dialkyl tin maleate.

5. A composition according to claim 4 wherein the dialkyl tin maleate is dibutyl tin maleate.

6. A composition according to claim 1 wherein the halogen containing resin is a vinyl chloride resin and the organo tin stabilizer is a dialkyl tin bis monobutyl maleate.

7. A composition according to claim 6 wherein the dialkyl tin bis monobutyl maleate is dibutyl tin bis monobutyl maleate.

8. A composition according to claim 1 wherein the halogen containing resin is a vinyl chloride resin and the rgano tin stabilizer is a dialkyl tin oxide wherein there are 4 to 10 carbon atoms in each alkyl group.

9. A composition according to claim 1 wherein the halogen containing resin is a vinyl chloride resin and the organo tin stabilizer is a dialkyl tin dilaurate.

10. A composition according to claim 9 wherein the dialkyl tin dilaurate is dibutyl tin dilaurate.

11. A composition according to claim 1 wherein the halogen containing resin is a vinyl chloride resin and the organo tin stabilizer is a dialkyl tin bis alkyl ester of a mercapto alkanoic acid having 2 to 3 carbon atoms.

12. A composition according to claim 1 wherein said halogen containing resin is a vinyl chloride resin and the organo tin stabilizer is a dialkyl tin dithio alkanoic acid alkyl ester wherein the thio alkanoic acid has 2 to 4 carbon atoms.

13. A heat resistant composition containing as a major constituent a vinyl chloride resin and as a stabilizer therefor a mixture of 0.01 to 10% of an organo tin stabilizer and 0.01 to 10% of a liquid polythiopolymercaptan.

14. A composition according to claim 13 wherein said liquid polythiopolymercaptan has a molecular weight of 500 to 700 and the general formula

$$HS(CH_2CH_2OCH_2OCH_2CH_2SS)_{2-4}CH_2CH_2OCH_2OCH_2CH_2SH$$

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